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(54) **Suede-like artificial leather**

Rauhlederartiges Kunstleder

Cuir artificiel ayant un aspect suédé

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## Description

[0001] This invention relates to a suede-like artificial leather which has good appearance and feeling, and also excels in color-developing property and pilling resistance, and a production process thereof.

[0002] Suede-like artificial leather, having a nap composed of fiber bundles which is formed on a surface of a substrate composed of the same fiber bundles and an elastomeric polymer, is known. Whereas, in the field of suede-like artificial leather, recently a high quality product is in demand, which satisfies all of such sensory requirements as the appearance (suede-like appearance), hand (soft touch) and color-developing property as well as physical requirement, e.g., pilling resistance.

[0003] More specifically, it is generally practiced to reduce the size of artificial leather-constituting fibers to microfine denier level, for the purpose of obtaining suede-like artificial leather of excellent appearance, but a leather containing such microfine denier fibers cannot be dyed to clear colors, but to only dull, whitish colors, being inferior in color developing property. It has also been practiced to substantially eliminate the elastomeric polymer from the interspaces among the individual fibers constituting each of the fiber bundles which constitute an artificial leather in order to render the hand of the leather extremely soft, pleasant one. When no elastomeric polymer is present in said inter-spaces (hereafter simply referred to as inside of the fiber bundles), however, the raised fibers are readily pulled out to aggravate the property which is normally referred to as pilling resistance.

[0004] Concerning improvement of color-developing property of suede-like artificial leather with a fibrous nap, various proposals have been made in the past. For example, Japanese Patent Publication JP-B-55-000506 proposed to apply an easy dyeable resin onto surfaces of a sheet with fibrous nap and to dye the sheet, and Japanese Patent Publications JP-B-61-025834 or JP-B-61-046592 proposed a method of dyeing artificial leather with a dyestuff which becomes water-soluble as reduced in the presence of an alkali, and then oxidizing the dye to fix it on the leather.

[0005] For improving pilling resistance of suede-like artificial leather with fibrous nap, Japanese Kokai (laid-open) Publication JP-A-57-154468 has proposed a method of dissolving a part of the polymer used in the leather with a solvent for the polymer, to fix the roots of the fibers forming the nap on the surface.

[0006] As microfine denier fiber bundles in which microfine fibers of differing deniers are mixed, Japanese Kokai (laid-open) Publication JP-A-63-243314 has disclosed a fibrous structure of blended yarn wherein the size distribution of island component satisfies the relationship of  $DC \approx 1.5DS$ , DS denoting the denier of the island component present within 1/4 of the radius from the outer periphery and DC denoting the denier of the island component present within 2/3 of the radius from the center point. Also a fibrous sheet whose microfine denier fiber bundles contain polyurethane within the bundles and ultrafine polyolefin fibers having an average diameter no greater than 1.0  $\mu\text{m}$  and an aspect ratio of 500 - 2200 are dispersed in the inside and around said bundles has been disclosed by Japanese Kokai JP-A-3-260150A. Japanese Kokai JP-A-5-156579A has disclosed a product and process according to the pre-characterising parts of claims 1 and 6, respectively, in particular a polyamide microfine denier fiber-forming fibers in which 0.02 - 0.2 denier fine fibers (A) and 0.001 - 0.01 denier microfine fibers (B) are dispersed as an island component, the weight ratio of (A)/(B) being 30/70 to 70/30; and suede-like artificial leather prepared from said fibers.

[0007] Such methods for improving color-developing property as described in above Publications JP-B-55-000506, JP-B-61-025834 and JP-B-61-046592 could improve the developing property per se, but degrade appearance and hand of the fibrous nap side of the product. Whereas, by the technology described in Kokai JP-A-63-243314, it is difficult to concurrently maintain good appearance and developing property, because in its product microfine denier fibers of different sizes are each localized and the technology is incapable of increasing the denier difference among the microfine fibers serving as the island components.

[0008] The technology described in Kokai JP-A-5-156579 achieves a minor improvement in developing property over the technology of Kokai JP-A-63-243314. However, due to high microfine denier fibers (B) content in the product a large number of microfine denier fibers are present on the napped surface and color-developing property of the product is yet insufficient. While it is possible to increase the product's developing property by selectively cutting and eliminating the microfine denier fibers on the napped surface under the severe conditions normally employed for napping the surfaces, the operation under such severe conditions injures and cuts also the fine fibers (A), resulting in failure to obtain suede-like artificial leather of favorable appearance.

[0009] Furthermore, by the method described in Kokai JP-A-57-154468, it cannot be avoided that the product has harder hand, because of the polyurethane present in inside the microfine denier fiber bundles.

[0010] The object of the present invention, therefore, is to provide a suede-like artificial leather having good appearance and hand and also excelling in color developing property and pilling resistance, and a process for making such a leather.

[0011] According to the present invention, as a product accomplishing the above object, provided is a suede-like artificial leather as defined in claim 1

[0012] The suede-like artificial leather of the present invention can be obtained by, for example, carrying out the process as defined in claim 6.

[0013] Examples of the polymers which constitute the island component in the microfibrillar-forming fibers (C) of the present invention, that is, the polymers for forming the fine fibers (A) and microfibrillar fibers (B), include melt-spinnable polyamides such as 6-nylon, 66-nylon, etc. and melt-spinnable polyesters such as polyethylene terephthalate, polybutylene terephthalate, cation-dyeable modified polyethylene terephthalate, etc. The fine fibers (A) and microfibrillar fibers (B) may be made of either a same polymer or different polymers.

[0014] Whereas, the polymer constituting the sea component has a different solubility or decomposability in solvents or decomposing agents from those of the island component (the sea component-forming polymer has the greater solubility or decomposability), has a low affinity with the island component, and exhibits a lower melt viscosity or less surface tension than those of the island component under spinning conditions. Examples of such polymers include easy-soluble polymers such as polyethylene, polystyrene, modified polystyrene, ethylene/propylene copolymers, etc. and easy-decomposable polymers such as polyethylene terephthalate which has been modified with sodium sulfoisophthalate, polyethylene glycol or the like.

[0015] The attached drawing shows a type of cross-section of a microfibrillar-forming fibers (C).

[0016] As illustrated in the drawing, the microfibrillar-forming fiber (C) contains in its sea component (1) two groups of fibers as the island component, i.e., fine fibers (A) of the greater average denier (1 denier = 9 tex) and microfibrillar fibers (B) of the less average denier, said fine fibers (A) and microfibrillar fibers (B) being approximately uniformly dispersed over the whole cross-sectional area of said fiber (C). That is, such fibers wherein fine fibers (A) and microfibrillar fibers (B) are unevenly distributed are unfit for use in the present invention. The fine fibers (A) and microfibrillar fibers (B) differ not only in average denier, but also in denier size of individual fibers constituting the respective groups to such an extent as allowing clear distinction.

[0017] Such a microfibrillar-forming fiber (C) can be obtained by a method comprising melting a mixture of a microfibrillar fibers (B)-forming polymer and a sea component polymer at a predetermined blend ratio, feeding the melt into a spinning machine concurrently with a melt of a fine fiber (A)-forming polymer which has been melted in a different melting system from the first, repeating joining and dividing of the melts at the spinning head several times to form a mixed system of the two and spinning the same; or by a method in which the two melts are combined and the fiber shape is defined at the spinneret portion, and then spun. That is, the fibers (C) are obtained by mixing the fiber (B)-forming polymer and the sea component polymer at a predetermined ratio and melting the mixture in a same melting system, and bi-component spinning the melt with another melt of fiber (A)-forming polymer in such a manner that the latter is approximately uniformly dispersed in the former.

[0018] As previously stated, fine fibers (A) and microfibrillar polymers (B) may be formed from a same polymer or from different polymers. However, the denier size of fine fibers (A) must range 0.02 - 0.2, while that of microfibrillar fibers (B) must be no more than 1/5 of average denier size of fibers (A) and less than 0.02 denier. Furthermore, the ratio between the number of fibers (A) and that of fibers (B) must be within a range of 2/1 to 2/3.

[0019] When the size of fine fibers (A) is less than 0.02 denier, the product exhibits insufficient color-developing property, while when it is greater than 0.2 denier, it becomes difficult to secure the high quality of appearance. Furthermore, it is preferred for fine fibers (A) to have an approximately uniform denier size, for achieving favorable appearance and hand. More specifically, it is preferred that the denier size ratio of the finest fiber (A) and the thickest fiber (A) within a fiber bundle is within a range of 1:1 - 1:3.

[0020] The microfibrillar fibers (B) are to entangle onto the fine fibers (A) to prevent pilling. In order to simultaneously accomplish retention of high quality appearance and securing of good developing property, the fibers (B) need to have a denier size not more than 1/5 of average denier size of fine fibers (A) and less than 0.02 denier; preferably between 1/10 and 1/50 of average denier size of fine fibers (A) and between 0.01 and 0.001 denier; still more preferably between 0.01 denier and 0.0015 denier. When the denier size of the microfibrillar fibers (B) is too low, only poor pilling preventing effect is obtained. Thus, the preferred lower limit is 0.001 denier, more preferably 0.0015 denier. Because the microfibrillar fibers (B) are formed by the method of melting the starting polymer in the same melting system with the sea component polymer as aforesaid, generally denier size variation among individual fibers is large. In the present invention, however, those fibers having the denier size not more than 1/5 of average denier size of fine fibers (A) and less than 0.02 denier are called the microfibrillar fibers (B).

[0021] The length of the microfibrillar fibers (B) is limited because they are obtained from a stream of molten mixed polymer, but preferably they should have a length of 5 mm or more, to achieve satisfactory pilling prevention. The length is controllable by selecting the combination of polymers in the occasion of spinning. When aforesaid polyester or polyamide polymers are used as the constituent, microfibrillar fibers (B) of sufficiently great length can be obtained.

[0022] According to the present invention, the fiber bundles preferably consist substantially of above-described fine fibers (A) and microfibrillar fibers (B) only, but presence of a minor amount of fibers not belonging to the scope of either (A) or (B) is permissible. It is preferred for favorable developing property as well as appearance that the number of fine fibers (A) present in a cross-section of single fiber bundle is within a range of 15 - 100.

[0023] According to the present invention, both fine fibers (A) and microfibrillar fibers (B) are mixedly present in the nap-forming fiber bundles before buffing. In the buffing step for forming nap, microfibrillar fibers (B) are more easily broken.

Consequently, the ratio between the strand numbers of fine fibers (A) and microfine fibers (B) at the outermost surface of the nap becomes greater than that in the substrate layer. Developing property of the product is affected by the fineness of the fibers present at the outermost surface part of the nap. Thus, the higher the ratio of fine fibers (A) present in said part, the better developing property can be obtained. It is necessary to obtain good developing property that the A/B ratio is at least 3/1. It is possible to reduce the number of microfine fibers (B) present in the outermost napped surface to substantially zero, by suitably selecting the napping treating conditions, and in that case the A/B ratio becomes infinite. Under ordinary industrial napping treating conditions, the A/B ratio is not greater than 100/1.

**[0024]** When the A/B ratio in the substrate layer is 2/1 or greater, the A/B ratio in the outermost napped surface becomes also high, which is preferred from the standpoint of developing property. Whereas, in such a case the pilling-preventing effect achieved by entanglement of microfine fibers (B) onto fine fibers (A) is drastically reduced, and the product will exhibit inferior pilling resistance. When the A/B ratio in the substrate layer is 2/3 or less, on the other hand, buffing must be slowly and repeatedly conducted in order to increase the A/B ratio at the napped surface to at least 3/1. This invites reduction in productivity. When the buffing is conducted under severe conditions to increase the productivity, not only the microfine fibers (B) but also the fine fibers (A) come to be broken, and a high quality suede-like product cannot be obtained. Thus, it is very important that the ratio between the strand numbers of fine fiber (A) and microfine fiber (B) (A/B) in the substrate is within the range of 2/1 to 2/3, in order to simultaneously achieve retention of high grade appearance and improvement in developing property and pilling resistance.

**[0025]** Denier size, strand number and length of microfine fibers (B) can be controlled by changing combination of such factors as the blend ratio of a polymer composing microfine fibers (B) and a sea component polymer, melt viscosity and surface tension. In general terms, a higher ratio of microfine fibers (B)-forming polymer results in a greater number of strands of the fibers (B), while their denier size remains about the same; and higher melt viscosity and surface tension tend to increase the denier size, decrease the strand number and shorten the fiber length. Based on those known tendencies, the denier size, strand number and fiber length of microfine fibers (B) in a fiber (C) can be predicted by test spinning at individual spinning temperature and spinning speed to be employed, as to any suitable combination of a microfine fiber-composing polymer and a sea component polymer.

**[0026]** The ratio of the sum of a fine fiber (A) component and microfine fiber (B) component in a microfine fiber-forming fiber (C) is preferably within a range of 40 - 80 % by weight, viewed from spinning stability and economy.

**[0027]** Microfine fiber-forming fibers (C) are processed to fibers of 2 - 10 deniers in size, if necessary through such steps as drawing, crimping, thermal setting and cutting. The terms, denier size and average denier size, as used herein can be readily determined from cross-sections of pertinent microfine fiber-forming fibers (C), i.e., by taking micrographs of the cross-sections, counting the numbers of the fine fibers (A) and microfine fibers (B), respectively, and dividing the respective weights of the fine fibers (A) and microfine fibers (B) in the 9000 m-long fiber (C) containing them by the numbers of the respective fibers. By a similar method denier sizes and average denier sizes of the fibers (A) and (B) can be readily determined from the fiber bundles composed of said fibers (A) and (B), after fibers (C) are converted into such fiber bundles. Concerning fiber length of microfine fibers (B), furthermore, it can be readily determined whether or not it is at least 5 mm, by treating the eventually produced suede-like artificial leather with dimethylformamide or the like to remove the elastomeric polymer therefrom, and observing the remaining fiber bundles with a microscope.

**[0028]** Microfine fiber-forming fibers (C) are opened with a card, passed through a webber to form random webs or cross-lap webs, and the resulting webs are laminated to an optional weight and thickness. The laminated webs are then subjected to a known entangling treatment such as needle punching, water-jet entanglement or the like, to be converted to a fiber-entangled non-woven fabric. If necessary, fibers other than the microfine fiber-forming fibers (C) may be added in a minor amount in the occasion of forming said non-woven fabric. Again if desired, a resin which can be dissolved away, for example, a polyvinyl alcohol-derived resin, may be applied to the non-woven fabric to provisionally set the same.

**[0029]** Then the non-woven fabric is impregnated with an elastomeric polymer and coagulated. The elastomeric polymer useful for this operation is, for example, a polyurethane obtained by reacting at least one polymer diol having an average molecular weight of 500 - 3,000 selected from the group comprising polyester diols, polyether diols, polyetherester diols, polycarbonate diols, etc.: at least one diisocyanate selected from aromatic, alicyclic and aliphatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, etc.; and at least one low molecular weight compound having at least two active hydrogen atoms, such as ethylene glycol, ethylenediamine, etc.; at prescribed mol ratios. Such a polyurethane can be used as a polyurethane composition, if necessary, by adding thereto such a polymer as synthesized rubber, polyester elastomer, or the like.

**[0030]** So formed polyurethane or a polyurethane composition is dispersed in a solvent or a dispersing agent, and the resulting polymer liquid is impregnated in the non-woven fabric. By treating the system then with a non-solvent of the polymer to effect wet coagulation, intended fibrous substrate is obtained. If required, such an additive or additives as a coloring agent, coagulation regulator, antioxidant, etc., may be blended into the polymer liquid. The amount of the polyurethane or polyurethane composition in the fibrous substrate is, as solid, preferably within a range of 10 - 50 % by weight.

**[0031]** The fibrous substrate is subsequently treated to convert fibres (C) into bundles of fibres (A) and (B), preferably by treating them with a liquid which is a non-solvent of the microfibre fiber component (B), fine fiber component (A) and the elastomeric polymer and is a solvent or a decomposing agent of the sea component in the fibres (C). As the liquid, toluene is used, for example, when said components (A) and (B) are nylon or polyethylene terephthalate and the sea component is polyethylene: and an aqueous caustic soda solution is used when said components (A) and (B) are nylon or polyethylene terephthalate and the sea component is an easy alkali-decomposable polyester. With this treatment the sea component polymer is removed from the microfibre fiber-forming fibers (C), leaving fiber bundles composed of the microfibre fibers (B) and fine fibers (A). Thus converted fiber bundles do not substantially contain the elastomeric polymer in their inside. When the non-woven fabric is provisionally set with a soluble and removable resin, the resin should necessarily be dissolved and removed before or after the above treating step.

**[0032]** The substrate is then sliced into plural sheets in the thickness direction, if necessary, and at least one of the surfaces of each sheet is given a napping treatment to form a napped surface composed chiefly of the fine and microfibre fibers, such that the ratio of fibres (A) to fibres (B) at the outermost surface of the nap is at least 3/1. For forming the napping surface, any known method such as buffing with a sand paper may be employed.

**[0033]** Thus obtained suede-like fibrous substrate is then dyed. The dyeing is carried out according to normal dyeing methods, using such dyestuffs composed mainly of acidic dyes, premetallized dyes, dispersed dyes, etc., depending on the kind of fibers present in the substrate. Dyed suede-like fibrous substrate is given a finish treatment or treatments such as rubbing, softening, brushing, etc. to provide suede-like artificial leather.

**[0034]** The suede-like artificial leather of the present invention has good appearance and hand and excels in developing property and pilling resistance. It is useful as materials for clothing, shoes, pouches, gloves and the like.

**[0035]** Hereinafter typical embodiments of the present invention are explained referring to specific working examples, it being understood that the invention is in no sense limited to these examples. In the examples, parts and percentages are by weight, unless specified otherwise.

#### Example 1

**[0036]** A melt formed by melting 5 parts of 6-nylon [microfibre fiber (B) component] and 35 parts of polyethylene in a same melting system, and another melt of 60 parts of 6 nylon [fine fiber (A) component], which was molten in a different melting system, were spun into microfibre fiber-forming fibers (C) having a size of 10 deniers, by a method of defining the fiber shape at the spinneret portion. The spinning conditions were so controlled that the number of fine fibers (A) present in the fiber (C) was 50. When cross-sections of said fibers (C) were observed, the average number of microfibre fibers (B) per a strand of fiber (C) was found to be about 50, and the fibers (A) and (B) were substantially uniformly dispersed.

**[0037]** Thus obtained fibers (C) were stretched by 3.0X, crimped, cut to a fiber length of 51 mm, opened with a card and formed into webs with a cross-lap webber. The webs were converted to a fiber-entangled non-woven fabric having a density of 650 g/m<sup>2</sup> by needle punching. During these steps the fibers showed autogeneous shrinkage and their size was reduced to about 4.5 deniers. The non-woven fabric was impregnated with a solution composed of 13 parts of a polyurethane composition whose chief component was a polyether-derived polyurethane and 87 parts of dimethylformamide (DMF), followed by coagulation and aqueous washing. Then the polyethylene in the fibers (C) was removed by extraction with toluene, to provide an about 1.3 mm-thick fibrous substrate consisting of 6-nylon fine and microfibre fiber bundles and polyurethane.

**[0038]** When cross-sections of these fiber bundles in the fibrous substrate were observed with an electron microscope, the average size of the fine fibers (A) was 0.054 denier, with substantially no denier variation; and the microfibre fibers (B) invariably had a size ranging between 0.01 denier and 0.001 denier, the average size being 0.0045 denier.

Also the most part of the microfibre fibers (B) had a length of at least 5 mm.

**[0039]** One of the surfaces of this substrate was buffed to be adjusted of its thickness to 1.20 mm, and thereafter the other surface was treated with an emery raising machine to form a napped surface in which the fine and microfibre fibers were raised. The substrate was then dyed with Irgalan Red 2GL (Chiba Geigy) at a concentration of 4 % owf. After subsequent finish treatments, the napped surface of the resultant suede-like artificial leather was enlarged by 500X with an electron microscope. When the so taken electron micrograph was observed, the ratio between the numbers of A to B was 8/1. The product exhibited excellent developing property, and very good appearance and hand.

#### Comparative Example 1

**[0040]** Thirty-five (35) parts of polyethylene and 65 parts of 6-nylon were separately melted in different systems, and together spun by a method of spinning while defining the fiber shape at the spinneret portion, in such a manner that the number of island component (6-nylon) fibers was 50. Except that thus obtained microfibre fiber-forming fibers of 10 deniers in size were used, the procedures of Example 1 were repeated to provide a dyed suede-like artificial leather.

[0041] An electron microscopic observation of cross-sections of the fiber bundles constituting the substrate of this suede-like artificial leather revealed that the average denier of 6-nylon fibers corresponding to fine fibers (A) was 0.063, and that substantially no fiber corresponding to the microfine fibers (B) was present.

[0042] The resulting product exhibited good developing property but inferior pilling resistance.

#### Comparative Example 2

[0043] A 10 denier size microfne fiber-forming fibers were obtained by a method of spinning while defining the fiber shape at the spinneret portion, by feeding to the spinning machine 15 parts of 6-nylon [microfne fiber (B) component] and 50 parts of polyethylene which were molten in a same melting system, and 35 parts of 6-nylon [fine fiber (A) component] which was molten in a separate system, in such a manner that the number of fine fibers (A) became 50. Except that so obtained microfne fiber-forming fibers were used, the procedures of Example 1 were repeated to provide a dyed suede-like artificial leather.

[0044] An electron microscopic observation of cross-sections of the fiber bundles constituting the substrate of this suede-like artificial leather revealed that the average size of the fine fibers (A) was 0.034 denier with substantially no variation in the denier size. Microfne fibers (B) invariably had a denier within the range of 0.007 - 0.001, the average denier being 0.004. Also when cross-sections of microfne fiber-forming fibers were observed with an electron microscope, the number of the microfne fibers (B) was about 180. A 500X enlarged electron micrograph of the napped surface of the resultant suede-like artificial leather revealed that the ratio in numbers of A to B was 2.2/1. The product exhibited drastically inferior developing property, while its pilling resistance was satisfactory.

#### Example 2

[0045] A melt formed by melting 5 parts of polyethylene terephthalate [microfne fiber (B) component] and 30 parts of polyethylene in a same melting system, and 65 parts of polyethylene terephthalate [fine fiber (A) component], which was molten in a different melting system, were spun into microfne fiber-forming fibers (C) having a size of 10 deniers, by a method of defining the fiber shape at the spinneret portion. The spinning conditions were so controlled that the number of fine fibers (A) present in the fiber (C) was 50. When cross-sections of said fibers (C) were observed in that occasion, the average number of microfne fibers (B) per a strand of fiber (C) was found to be about 50, and the fibers (A) and (B) were substantially uniformly dispersed.

[0046] Thus obtained fibers (C) were stretched by 3.0X, crimped, cut into 51 mm-long fibers, opened with a card, and converted into webs with a cross-lap webber. The webs were subjected to a needle punching treatment, caused to shrink by 40 % in area in hot water, and formed into a fiber-entangled non-woven fabric having a density of 820 g/m<sup>2</sup>. The non-woven fabric was impregnated with a solution composed of 13 parts of a polyurethane composition whose chief component was a polyether-derived polyurethane and 87 parts of DMF, followed by coagulation and aqueous washing. Then the polyethylene in the fibers (C) was removed by extraction with toluene, to provide a 1.3 mm-thick fibrous substrate consisting of polyethylene terephthalate fine and microfne fiber bundles and polyurethane.

[0047] When cross-sections of the fiber bundles in the fibrous substrate were observed with an electron microscope, the average denier of fine fibers (A) was 0.060 denier, with substantially no denier variation; and the microfne fibers (B) invariably had a size ranging between 0.01 and 0.0015 denier, the average size being 0.005 denier. No polyurethane was contained inside the fine and microfne fiber bundles. Also the length of the microfne fibers (B) was predominantly no less than 5 mm.

[0048] One of the surfaces of this substrate was buffed to be adjusted of its thickness to 1.20 mm, and then the other surface was treated with an emery raising machine to form a napped surface in which the fine and microfne fibers were raised. The substrate was dyed with Resolin Blue 2BRS at a concentration of 2 % OWf. The dye deposited on the polyurethane was reduction cleared and the product was finished. The napped surface of the resulting suede-like artificial leather was enlarged by 500X with an electron microscope. When the so taken electron micrograph was observed, the ratio between the numbers of A to B was 8/1. The product exhibited excellent developing property and very good appearance as well as hand.

#### Comparative Example 3

[0049] A 10 denier size microfne fiber-forming fibers were obtained by a method of spinning while defining the fiber shape at the spinneret portion, by feeding to the spinning machine 5 parts of polypropylene [microfne fiber (B) component] and 35 parts of polyurethane which were molten in a same melting system, and 60 parts of 6-nylon [fine fiber (A) component] which was molten in a separate system, in such a manner that the number of fine fibers (A) present in the microfne fiber-forming fiber was 50. When cross sections of the fibers were observed in that occasion, the average number of microfne fibers (B) present in the formed fiber was about 100, and the fibers (A) and (B) were approximately

uniformly dispersed.

[0050] The resultant fibers were stretched by 3.0X, crimped, cut to a length of 51 mm, opened with a card, and formed into webs with a cross-lap webber. The webs were then made into a fiber-entangled non-woven fabric having a density of 600 g/m<sup>2</sup> by needle punching. The non-woven fabric was impregnated with a solution composed of 4 parts of a polyurethane composition whose chief component was a polyether-derived polyurethane and 96 parts of DMF, coagulated and washed with water. Thus a 1.3 mm-thick fibrous substrate was obtained. The polyurethane in the micro-fine fiber-forming fibers was at least partially dissolved in situ by the DMF during the above impregnation step, but was solidified again during the subsequent coagulation step.

[0051] When cross-sections of the fiber bundles in the fibrous substrate were observed with an electron microscope, average denier of fine fibers (A) was found to be 0.058, with substantially no denier variation; and that of the microfine fibers (B) was 0.003. In the interspaces among the microfine fibers in the fiber bundles, polyurethane was present in porous state.

[0052] This fibrous substrate was processed in the identical manner with Example 1 to be finished to a dyed, suede-like artificial leather.

[0053] The resulting product exhibited good developing property, but had a hard hand because the microfine fibers in the fiber bundles were mutually fixed with the polyurethane, i.e., because the polyurethane, an elastomeric polymer, was contained inside the fiber bundles. Also the appearance still left room for further improvement.

[0054] The test results of the suede-like artificial leathers which were obtained in above Examples and Comparable Examples are tabulated in Table 1 below.

TABLE 1

	Within a Fiber Bundle				Raised Surface		Sensory Test		3) Pilling (grade)
	Fine fiber (A) (average dr.)	Microfine fiber (B) (average dr.)	Ratio of fiber numbers (A/B)	Ratio of fiber numbers (A/B)	Ratio of fiber numbers (A/B)	1) K/S	Appear- ance	Feeling	
Example 1	0.054	0.0045	1/1	8/1	15.6	o	o	o	4
Comparative Example 1	0.063	-	-	-	16.5	△	△	o	3
Comparative Example 2	0.034	0.004	1/3.6	2.2/1	10.5	o	o	o	4 - 5
Example 2	0.060	0.005	1/1	8/1	14.5	o	o	o	4
Comparative Example 3	0.058	0.003	1/2.0		14.8	△	△	x	3 - 4



1) Calculated by inserting the surface reflectivity R into the following equation:

$$K/S = (1-R)^2/2R$$

2) Evaluated by randomly selected 20 panelers following the standards below:

o : good

Δ : less satisfactory

x : poor

3) Condition of each product after being treated with a pilling tester for 20 hours was observed.

4) A 500X magnified electron micrograph was taken of each sample and visible numbers of raised fibers within an optionally selected 100 μm x 100 μm area in each micrograph were counted and the average values were calculated.

#### Claims

1. A suede-like artificial leather whose substrate is composed of fiber bundles composed of fine fibers and microfine fibers, and an elastomeric polymer, said fine and microfine fibers being approximately uniformly dispersed over the cross-section of the fiber bundles, said fiber bundles not containing the elastomeric polymer in the interspaces among the individual fibers constituting each of the fiber bundles, said substrate having a nap on its surface composed of said fiber bundles, and being dyed, which leather is characterized in that said fiber bundles constituting the substrate are composed of fine fibers (A) having a fineness of 0.0022 - 0.022 tex (0.02 - 0.2 denier) and microfine fibers (B) having a fineness not more than 1/5 of the average fineness of the fine fibers (A) and less than 0.0022 tex (0.02 denier), the ratio between the number of fine fibers (A) and that of the microfine fibers (B) ranging from 2/1 to 2/3, and the ratio between the number of fine fibers (A) and that of the microfine fibers (B) at the outermost surface of the nap being at least 3/1.
2. A suede-like artificial leather as described in Claim 1, in which the fineness of the microfine fibers (B) is between 1/10 to 1/50 of that of the average fineness of the fine fibers (A) and ranges from 0.001 - 0.0001 tex (0.01 - 0.001 denier).
3. A suede-like artificial leather as described in Claim 1, in which the fineness of the microfine fibers (B) is between 1/10 to 1/50 of that of the average fineness of the fine fibers (A) and ranges from 0.001 - 0.00017 tex (0.01 - 0.0015 denier).
4. A suede-like artificial leather as described in Claim 1, in which the fine fibers (A) and microfine fibers (B) are composed of melt-spinnable polyamides or melt-spinnable polyesters.
5. A suede-like artificial leather as described in Claim 1, in which the elastomeric polymer is a polyurethane.
6. A method of manufacturing suede-like artificial leather whose substrate is composed of fiber bundles and an elastomeric polymer, said substrate having nap on its surface composed of said fiber bundles and being dyed, which comprises carrying out the following steps by the stated order:

(a) a step for making a fine fiber- and microfine fiber-forming fibers (C) which are composed of a sea component polymer removable by dissolution or decomposition and island components comprising fine fibers (A) and microfine fibers (B), said island components being present as dispersed in cross-sections of said fibers (C), and said fine and microfine fibers being approximately uniformly dispersed over the cross section of the fiber bundle,

(b) a step for making an entangled non-woven fabric composed of said fibers (C),

(c) a step for impregnating the non-woven fabric with an elastomeric polymer liquid and wet coagulating the same to form a substrate,

(d) a step for converting said fibers (C) into fiber bundles composed of said fine fibers (A) and microfine fibers (B),

(e) a step for forming a nap on at least one surface of said substrate, and

(f) a step for dyeing the resulting napped nonwoven fabric, characterised in that

said fine fibres (A) have a fineness ranging 0.0022 - 0.022 tex (0.02 - 0.2 denier),

said microfine fibres (B) have a fineness no more than 1/5 of the average fineness of said fibres (A) and less than 0.0022 tex (0.2 denier),

said fibres (C) being convertible into fibre bundles containing said fine fibres (A) and microfine fibres (B) at a strand number ratio of  $A/B = 2/1$  to  $2/3$ , and in that the ratio between the of fine fibres (A) and that of microfine fibres (B) at the outermost surface of the nap formed in step (e) is at least 3/1.

7. A method as described in Claim 6, in which the fineness of microfine fibers (B) is between 1/10 to 1/50 of the average fineness of said fine fibers (A) and also is within a range of 0.001 - 0.0001 tex (0.01 - 0.001 denier).

8. A method as described in Claim 6, in which the fineness of microfine fibers (B) is between 1/10 to 1/50 of the average fineness of fine fibers (A), and also is between 0.001 - 0.00017 tex (0.01 - 0.0015 denier).

9. A method as described in Claim 6, in which said fine fibers (A) and microfine fibers (B) are composed of melt-spinnable polyamides or melt-spinnable polyesters.

10. A method as described in Claim 6, in which said elastomeric polymer is a polyurethane.

11. A method as described in Claim 6, in which the sea component is selected from the group consisting of polyethylene, polystyrene, modified polystyrene, ethylene/propylene copolymers, polyethylene terephthalate modified with sodium sulfoisophthalate and polyethylene terephthalate modified with polyethylene glycol.

12. A method as described in Claim 6, in which the product of the step (c) is treated with a liquid, which is a non-solvent of said fine fibers (A), microfine fibers (B) and the elastomeric polymer but is a solvent or decomposing agent of the sea component polymer, in the step (d), whereby the sea component polymer is removed from said product and the fibers (C) are converted into fiber bundles composed of the fine fibers (A) and microfine fibers (B).

## Patentansprüche

1. Rauhlederartiges Kunstleder, dessen Substrat aus Faserbündeln aus feinen Fasern und mikrofeinen Fasern und einem elastomeren Polymer zusammengesetzt ist, wobei die feinen und mikrofeinen Fasern näherungsweise gleichförmig über den Querschnitt der Faserbündel verteilt sind, die Faserbündel in den Zwischenräumen zwischen den einzelnen Fasern, die jedes Faserbündel aufbauen, das elastomere Polymer nicht enthalten, das Substrat an seiner Oberfläche einen Flor aus den Faserbündeln besitzt und gefärbt ist, wobei das Leder dadurch gekennzeichnet ist, daß die das Substrat aufbauenden Faserbündel aus feinen Fasern (A) mit einer Feinheit von 0,0022 bis 0,022 tex (0,02 bis 0,2 Denier) und mikrofeinen Fasern (B) mit einer Feinheit von nicht mehr als 1/5 der mittleren Feinheit der feinen Fasern (A) und weniger als 0,0022 tex (0,02 Denier) zusammengesetzt sind, wobei das Verhältnis zwischen der Anzahl feiner Fasern (A) und der Anzahl der mikrofeinen Fasern (B) im Bereich von 2/1 bis 2/3 liegt und das Verhältnis zwischen der Anzahl feiner Fasern (A) und der Anzahl der mikrofeinen Fasern (B) an der äußersten Oberfläche des Flors mindestens 3/1 beträgt.

2. Rauhlederartiges Kunstleder nach Anspruch 1, wobei die Feinheit der mikrofeinen Fasern (B) zwischen 1/10 und 1/50 der mittleren Feinheit der feinen Fasern (A) beträgt und im Bereich von 0,001 bis 0,0001 tex (0,01 bis 0,001 Denier) liegt.

3. Rauhlederartiges Kunstleder nach Anspruch 1, wobei die Feinheit der mikrofeinen Fasern (B) zwischen 1/10 und 1/50 der mittleren Feinheit der feinen Fasern (A) beträgt und im Bereich von 0,001 bis 0,00017 tex (0,01 bis 0,0015 Denier) liegt.
- 5 4. Rauhlederartiges Kunstleder nach Anspruch 1, wobei die feinen Fasern (A) und mikrofeinen Fasern (B) aus schmelzverspinnbaren Polyamiden oder schmelzverspinnbaren Polyestern bestehen.
5. Rauhlederartiges Kunstleder nach Anspruch 1, wobei das elastomere Polymer ein Polyurethan ist.
- 10 6. Verfahren zur Herstellung eines rauhlederartigen Kunstleders, dessen Substrat aus Faserbündeln und einem elastomeren Polymer zusammengesetzt ist, wobei das Substrat auf seiner Oberfläche einen Flor aus den Faserbündeln besitzt und gefärbt ist, welches das Ausführen der folgenden Stufen in der angegebenen Reihenfolge umfaßt:
  - 15 (a) eine Stufe zur Herstellung von feinen Fasern und mikrofeinen Fasern bildenden Fasern (C), die aus einem durch Auflösung oder Zersetzung entfernbaren "Meer"-Komponenten-Polymer und "Insel"-Komponenten, umfassend feine Fasern (A) zusammengesetzt sind, wobei die "Insel"-Komponenten verteilt über den Querschnitt der Fasern (C) vorliegen und die feinen und mikrofeinen Fasern näherungsweise gleichförmig über den Querschnitt des Faserbündels verteilt sind,
  - 20 (b) eine Stufe zur Herstellung eines gewirkten bzw. verschlungenen Faservlieses aus den Fasern (C),
  - (c) eine Stufe zur Imprägnierung des Faservlieses mit einer Flüssigkeit eines elastomeren Polymers und zur Naßkoagulation derselben, um ein Substrat zu bilden,
  - 25 (d) eine Stufe zur Umwandlung der Fasern (C) in Faserbündel aus den feinen Fasern (A) und den mikrofeinen Fasern (B),
  - (e) eine Stufe zur Bildung eines Flors auf mindestens einer Oberfläche des Substrats, und
  - 30 (f) eine Stufe zum Färben des resultierenden angerauchten Faservlieses, dadurch **gekennzeichnet**, daß die feinen Fasern (A) eine Feinheit im Bereich von 0,0022 bis 0,022 tex (0,02 bis 0,2 Denier) besitzen, die mikrofeinen Fasern (B) eine Feinheit von nicht mehr als 1/5 der mittleren Feinheit der Fasern (A) und weniger als 0,002 tex (0,2 Denier) besitzen, die Fasern (C) umwandelbar sind in Faserbündel, die die feinen Fasern (A) und mikrofeinen Fasern (B) in einem Strangzahl-Verhältnis von A/B = 2/1 bis 2/3
  - 35 enthalten und dadurch, daß das Verhältnis zwischen der Anzahl feiner Fasern (A) und der Anzahl mikrofeiner Fasern (B) an der äußersten Oberfläche des in der Stufe (e) gebildeten Flors mindestens 3/1 beträgt.
7. Verfahren nach Anspruch 6, wobei die Feinheit der mikrofeinen Fasern (B) zwischen 1/10 und 1/50 der mittleren Feinheit der feinen Fasern (A) liegt und außerdem im Bereich vom 0,001 bis 0,0001 tex (0,01 bis 0,001 Denier) liegt.
- 40 8. Verfahren nach Anspruch 6, wobei die Feinheit der mikrofeinen Fasern (B) zwischen 1/10 und 1/50 der mittleren Feinheit der feinen Fasern (A) liegt und außerdem zwischen 0,001 und 0,00017 tex (0,01 bis 0,0015 Denier) liegt.
- 45 9. Verfahren nach Anspruch 6, wobei die feinen Fasern (A) und mikrofeinen Fasern (B) aus schmelzverspinnbaren Polyamiden oder schmelzverspinnbaren Polyestern bestehen.
10. Verfahren nach Anspruch 6, wobei das elastomere Polymer ein Polyurethan ist.
- 50 11. Verfahren nach Anspruch 6, wobei die "Meer"-Komponente ausgewählt ist aus der Gruppe bestehend aus Polyethylen, Polystyrol, modifiziertem Polystyrol, Ethylen/Propylencopolymeren, mit Natriumsulfoisophthalat modifiziertem Polyethylenterephthalat und mit Polyethylenglykol modifiziertem Polyethylenterephthalat.
- 55 12. Verfahren nach Anspruch 6, wobei das Produkt der Stufe (c) mit einer Flüssigkeit behandelt wird, die ein Nicht-Lösungsmittel für die feinen Fasern (A), mikrofeinen Fasern (B) und das elastomere Polymer ist, aber ein Lösungsmittel oder Zersetzungsmittel für das "Meer"-Komponenten-Polymer ist in der Stufe (d), wodurch das "Meer"-Komponenten-Polymer aus dem genannten Produkt entfernt wird und die Fasern (C) in Faserbündel aus den feinen Fasern (A) und mikrofeinen Fasern (B) umgewandelt werden.

## Revendications

1. Cuir artificiel semblable à du suède dont le substrat est composé de faisceaux de fibres composés de fibres fines et de fibres microfines et d'un polymère élastomère, lesdites fibres fines et microfines étant dispersées à peu près uniformément sur la section transversale des faisceaux de fibres, lesdits faisceaux de fibres ne contenant pas le polymère élastomère dans les espaces intermédiaires entre les fibres individuelles constituant chacun des faisceaux de fibres, ledit substrat comportant une nappe sur sa surface composée desdits faisceaux de fibres, et étant teinté, lequel cuir est caractérisé en ce que lesdits faisceaux de fibres constituant le substrat sont composés de fibres fines (A) présentant une finesse de 0,0022 à 0,022 tex (0,02 à 0,2 denier) et de fibres microfines (B) présentant une finesse n'étant pas supérieure à 1/5 de la finesse moyenne des fibres fines (A) et étant inférieure à 0,0022 tex (0,02 denier), le rapport entre le nombre de fibres fines (A) et celui des fibres microfines (B) allant de 2/1 à 2/3, et le rapport entre le nombre de fibres fines (A) et celui des fibres microfines (B) au niveau de la surface la plus extérieure de la nappe étant d'au moins 3/1.
2. Cuir artificiel semblable à du suède comme décrit dans la revendication 1, dans lequel la finesse des fibres microfines (B) est entre 1/10 à 1/50 de celle de la finesse moyenne des fibres fines (A) et va de 0,001 à 0,0001 tex (0,01 à 0,001 denier).
3. Cuir artificiel semblable à du suède comme décrit dans la revendication 1, dans lequel la finesse des fibres microfines (B) est entre 1/10 à 1/50 de celle de la finesse moyenne des fibres fines (A) et va de 0,001 à 0,00017 tex (0,01 à 0,0015 denier).
4. Cuir artificiel semblable à du suède comme décrit dans la revendication 1, dans lequel les fibres fines (A) et les fibres microfines (B) sont composées de polyamides pouvant être filés à chaud ou de polyesters pouvant être filés à chaud.
5. Cuir artificiel semblable à du suède comme décrit dans la revendication 1, dans lequel le polymère élastomère est un polyuréthane.
6. Procédé de fabrication d'un cuir artificiel semblable à du suède dont le substrat est composé de faisceaux de fibres et d'un polymère élastomère, ledit substrat comportant une nappe sur sa surface composée desdits faisceaux de fibres et étant teint, qui comprend l'exécution des étapes suivantes suivant l'ordre énoncé :
  - (a) une étape destinée à fabriquer des fibres (C) formant des fibres fines et des fibres microfines qui sont composées d'un polymère de composant de mer pouvant être éliminé par dissolution ou décomposition et des composants formant des îlots comprenant des fibres fines (A) et des fibres microfines (B), lesdits composants formant des îlots étant présents sous forme dispersée dans les sections transversales desdites fibres (C), et lesdites fibres fines et microfines étant dispersées à peu près uniformément sur la section transversale du faisceau de fibres,
  - (b) une étape destinée à fabriquer une étoffe non tissée enchevêtrée composée desdites fibres (C),
  - (c) une étape destinée à imprégner l'étoffe non tissée d'un liquide de polymère élastomère et à coaguler au mouillé celle-ci afin de former un substrat,
  - (d) une étape destinée à convertir lesdites fibres (C) en faisceaux de fibres composés desdites fibres fines (A) et fibres microfines (B),
  - (e) une étape destinée à former une nappe sur au moins une surface dudit substrat, et
  - (f) une étape destinée à teindre l'étoffe non tissée nappée résultante, caractérisé en ce que lesdites fibres fines (A) présentent une finesse allant de 0,0022 à 0,022 tex (0,02 à 0,2 denier), lesdites fibres microfines (B) présentent une finesse n'étant pas supérieure à 1/5 de la finesse moyenne desdites fibres (A) et étant inférieure à 0,0022 tex (0,2 denier), lesdites fibres (C) étant convertibles en faisceaux de fibres contenant lesdites fibres fines (A) et fibres microfines (B) suivant un rapport de nombre de brins de  $A/B = 2/1$  à  $2/3$ , et en ce que le rapport entre le nombre de fibres fines (A) et celui de fibres microfines (B) au niveau de la surface la plus extérieure de la nappe formée au cours de l'étape (e) est d'au moins 3/1.
7. Procédé comme décrit dans la revendication 6, dans lequel la finesse des fibres microfines (B) est entre 1/10 à 1/50 de la finesse moyenne desdites fibres fines (A) et est également à l'intérieur d'une plage de 0,001 à 0,0001 tex (0,01 à 0,001 denier).

8. Procédé comme décrit dans la revendication 6, dans lequel la finesse des fibres microfines (B) est entre 1/10 à 1/50 de la finesse moyenne des fibres fines (A), et est également entre 0,001 à 0,00017 tex (0,01 à 0,0015 denier).
9. Procédé comme décrit dans la revendication 6, dans lequel lesdites fibres fines (A) et fibres microfines (B) sont composées de polyamides pouvant être filés à chaud ou de polyesters pouvant être filés à chaud.
10. Procédé comme décrit dans la revendication 6, dans lequel ledit polymère élastomère est un polyuréthane.
11. Procédé comme décrit dans la revendication 6, dans lequel le composant de mer est choisi parmi le groupe constitué d'un polyéthylène, un polystyrène, un polystyrène modifié, des copolymères éthylène/propylène, un polyté-réphthalate d'éthylène modifié par du sulfo-isophtalate de sodium et un polyté-réphthalate d'éthylène modifié par du polyéthylèneglycol.
12. Procédé comme décrit dans la revendication 6, dans lequel le produit de l'étape (c) est traité par un liquide, qui est un non solvant desdites fibres fines (A), fibres microfines (B) et du polymère élastomère mais est un solvant ou un agent de décomposition du polymère de composant de mer, dans l'étape (d), grâce à quoi le polymère de composant de mer est éliminé dudit produit et les fibres (C) sont converties en faisceaux de fibres composés des fibres fines (A) et fibres microfines (B).

FIG. 1

